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Carbon nanotubes: enhancing the polymer building blocks for intelligent materials

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Carbon nanotubes: enhancing the polymer building blocks for intelligent materials

Abstract

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Keywords

Carbon, nanotubes, enhancing, polymer, building, blocks, for, intelligent, materials

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Carbon nanotubes: enhancing the polymer building blocks for intelligent materials

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Electroactive polymers can be engineered at the molecular level to recognise external stimuli, they are conductive and they are capable of localised processing. These are properties which make them ideal building blocks for intelligent materials. This article investigates the suitability of carbon nanotubes for enhancing (polymer) building blocks for intelligent materials.

1. Introduction

Intelligent or smart materials are under active investigation for their potential applications in health monitoring, space exploration, civil engineering, automotive, aerospace, textiles and the battlefield of the future. For the purpose of this article, an intelligent material is defined as proposed by Wallace *et al.*: "An intelligent material is capable of recognising appropriate environmental stimuli, processing the information arising from the stimuli and responding to it in an appropriate manner and time frame".¹ Intelligent materials differentiate themselves from conventional materials by their dynamic character, which allows them to respond autonomously to changing environmental conditions.²

Nature has spent billions of years assembling building blocks (such as lipids, peptides and nucleic acids) into complex, functional and (sometimes) intelligent entities. Selectivity and recognition at the molecular scale, such as, for example, antibody–antigen interactions, is a critical feature of living systems. Hence the identification of molecular building blocks whose chemical and electrical properties can

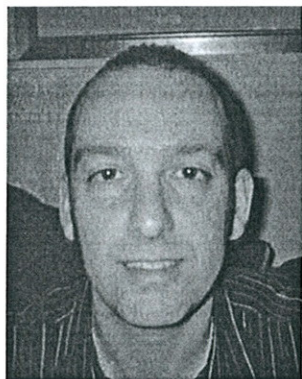
be manipulated and controlled is a fundamental requirement for the synthetic assembly of intelligent materials. Conducting electroactive polymers (CEPs), such as the polyanilines (PAns), polypyrroles (PPys) and polythiophenes (PThs), have been recognised as suitable building blocks as they can be engineered at the molecular level to recognise external stimuli, they are conductive and they are capable of localised processing.¹ In addition, it is well-known that significant changes can be observed in properties such as conductivity, volume and colour upon electrical stimulation. In short (see ref. 1 for further details), PPys and PThs exist in two oxidation states enabling reversible switching between (doped) oxidized forms (with good electrical conductivity) and reduced forms (with very low conductivity), see Scheme 1. PAns exist in three different oxidation states (leucoemeraldine, emeraldine and pernigraniline) which can be switched not only by electrical stimulation (like PPy/PTh), but also through addition of acid or base. Only one of these three states (emeraldine salt) is electrically conducting and can be de-doped to the non-conducting emeraldine base form. This ability to switch is of particular importance for the dynamic requirement allowing materials to display 'intelligence'.

The synthesis of PAn, PPy and PTh has been extensively reviewed^{1,3–7} and their main properties have been summarised in Table 1 (compiled from refs. 8–36).

Conducting electroactive materials are ideal candidates for organic electronics,^{37,38} and electrically conducting textiles.^{39,40} The conductivity values for (as-prepared) polymeric films are *ca.* 100 S cm^{−1} (PPy),⁴¹ while films prepared using a substituted thiophene monomer resulted in significant changes in conductivity, from 170 S cm^{−1} for PTh to 500 S cm^{−1} for poly(3-methylthiophene).⁴² In an important recent development, Lee *et al.*¹⁵ have shown metallic transport in free-standing films of PAn using self-stabilised dispersion polymerisation.⁴³ The reported room temperature conductivity of 1300 S cm^{−1}¹⁵ is a significant improvement compared to 400 S cm^{−1} for films prepared *via* the standard method.⁴⁴

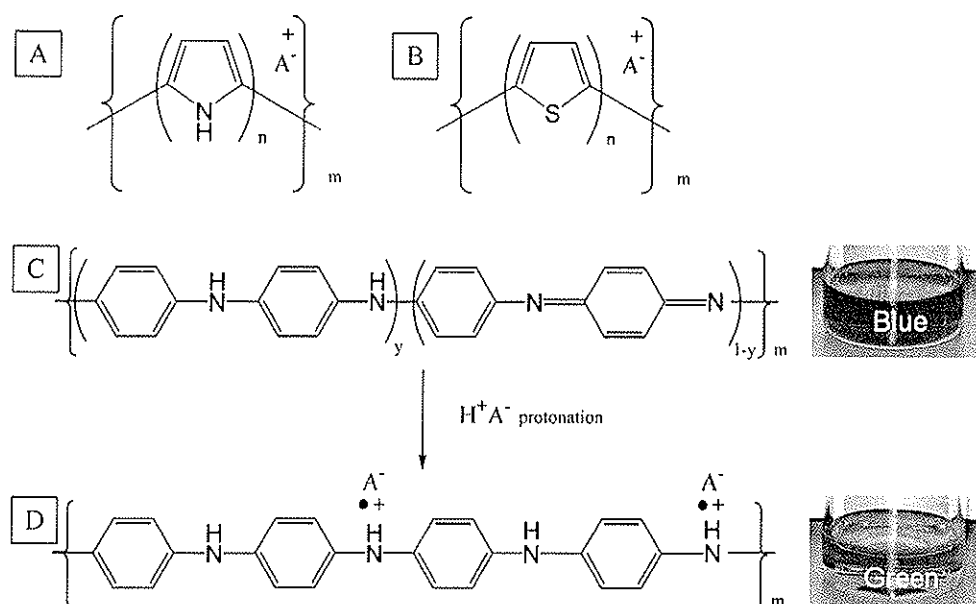
Alignment of polymer chains by drawing resulted in significant increases in the conductivity of films (increase from 300 to 1 × 10³ S cm^{−1}⁴⁵) and fibres (increase from 100 to 1.9 × 10³ S cm^{−1}¹⁶). Other characteristics include the mobility of charge carriers (0.6 cm² V^{−1} s^{−1} for modified PTh films²⁰) and current carrying capacity (100 A cm^{−2} for PAn films²²).

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Scheme 1 Structure of polypyrroles (A), polythiophenes (B), and polyanilines (C). n , A^- , and m indicate the number of monomers per unit positive charge, counter ion, and number of repeat units, respectively. The polyaniline oxidation states are determined by y : leucoemeraldine ($y = 1$), emeraldine ($y = 0.5$) and pernigraniline ($y = 0$). Example of switching (by protonation) between non-conducting (C) and conducting (D) forms of polyaniline, including corresponding colour changes (blue to green).

Table 1 Summary and comparison of conducting electroactive polymers (polyanilines, polypyrroles, polythiophenes) and carbon nanotube properties displayed (where appropriate) for single molecules and for processed materials such as films, fibres or networks. PAn, PPy and PTh, denote polyaniline, polypyrrole and polythiophene respectively

Property	Electroactive polymers	Carbon nanotubes
Engineering (functionalisation)	'Easy' ^{1,8,9}	'Easy' ¹⁰⁻¹³
Conductivity/S cm ⁻¹	Nanotube: $\approx 10^3$ (PPy ¹⁴) Film: 1.3×10^3 (PAn ¹⁵) Fibre: 2×10^3 (PAn ¹⁶)	Single: $>1 \times 10^6$ ^{a, 17} Network: 3.5×10^3 ^{b, 18} Fibre: 5×10^3 ¹⁹
Charge carrier mobility/cm ² V ⁻¹ s ⁻¹	0.6 (PTh ²⁰)	10^5 ²¹
Current carrying capacity/A cm ⁻²	100 (PAn ²²)	10^9 ²³
Young's modulus/GPa	Film: 8.5 (PTh ²⁴) Fibre: 3.4 (PAn ²⁵) Film: 0.27 (PTh ²⁴) Fibre: 0.2 (PAn ²⁵)	Single: 1000 ²⁶ Bundle: 640 ^{27,28} Fibre: 80 ^{c, 29}
Tensile strength/GPa	Film: 0.27 (PTh ²⁴) Fibre: 0.2 (PAn ²⁵)	Single: 37 ³⁰ Fibre: 0.46, ^{d, 31} 1.8 ^{c, 29}
Actuation (isometric stress)/MPa	5 (PAn ^{c, 33})	26 ³³
Optical activity	Induced ^{d,34-36}	Inherent ^e

^a Measured resistance $R \approx 32$ k Ω (at 290 K) for a metallic single-walled nanotube ($l = 4$ μ m, $d = 1.7$ nm), yielding a conductivity, $\sigma = 0.9 \times 10^6$ S cm⁻¹, obtained using $\sigma = l/R \cdot A$. The area, $A = 1.45$ nm², is evaluated from the width of a single shell of carbon atoms. ^b Nanotube network doped with SOCl₂. ^c Fibres produced from spinning, with poly(vinyl alcohol) used as coagulant. ^d Fibres drawn from a catalytic chemical vapour deposition grown forest of multi-walled carbon nanotubes. ^e Isometric stress during cyclic voltammetry cycling: during square wave cycling isometric stress was 3.3 MPa. ^f Optical activity is induced through either addition of chiral dopants (PAn) or covalent attachment of chiral substituents (PPy, PTh). ^g Each carbon nanotube is uniquely specified by its chiral vector (defined in terms of graphene sheet unit vectors) $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where n and m are integers and its chiral angle (defined as the angle between the unit vector \vec{a}_1 and the chiral vector \vec{C}_h). Hence, carbon nanotubes for which $n \neq m$, and n or $m \neq 0$, should exhibit optical activity.

The ability to actuate is an important aspect of the building blocks for intelligent materials. A comprehensive review of actuators based on conducting polymers was collected by Smela.⁴⁶ Actuator peak performance is thought to be closely related to mechanical properties, as postulated by Baughman.⁴⁷ The highest mechanical properties have been reported for polythiophene films exhibiting Young's modulus, $Y = 8.5$ GPa, and tensile strength, $T = 0.3$ GPa.²⁴ The properties of the other polymers are in the same order of magnitude; $Y = 3.4$ GPa, $T = 0.2$ GPa for PAn,²⁵ and

$Y = 4.3$ GPa, $T = 0.1$ GPa for PPy.¹ Significantly higher mechanical properties have been reported for other polymeric materials such as poly(2,5-dimethoxy-*p*-phenylenevinylene) ($Y = 35$ GPa, $T = 0.7$ GPa)⁴⁸ and polyacetylene ($Y = 100$ GPa, $T = 0.9$ GPa).⁴⁹ Table 1 measures actuator performance in terms of isometric stress, *i.e.* stress generated by actuator at constant length. Other measures of actuator performance include isotonic strain (strain under constant applied load), work per cycle, cycle switching speeds and life time. For example, measurable actuation has been observed

for isotonic loads of 8 MPa (PPy fibre),⁵⁰ 22 MPa (PPy film),⁵¹ and 90 MPa (PAn fibre),⁵² whereas fast cycle switching speeds and enhanced life times without failure ($>10^6$ cycles) have been reported for PAn fibre actuators in ionic liquids,²⁵ e.g. PANION PAn fibre, see Fig. 1.

Many pharmaceutically active molecules are chiral, with each of the enantiomers exhibiting different biological effects. For example, one form of ketamine is a sedative, while the other enantiomer is a hallucinogenic. Considerable effort is directed towards efficient methods for producing enantiomerically pure compounds, see the recent review by Canary and co-workers.⁵³ Applications include chiral films or membranes for enantioseparation,^{54,55} and chiral coatings for controlled release of pharmaceutical or agrochemical products. Optical activity is not inherent to our polymers but is induced through addition of chiral dopants (in PAn),³⁴ or covalent attachment of chiral substituents (in PPy and PTh).^{35,36} It has been suggested that the optical activity arising from adoption of either a one-handed helical conformation or a helical packing of polymer chains (see review on PTh optical activity by Meijer and co-workers⁵⁶). The optical activity of PAn in

various forms and oxidation states has been thoroughly investigated by Kane-Maguire and Wallace.^{34,57-62}

The following well-known values of common materials can be used to put the properties of CEPs displayed in Table 1 into perspective: conductivity of copper ($1 \times 10^6 \text{ S cm}^{-1}$), the current carrying capacity of metals ($1 \times 10^5 \text{ A cm}^{-2}$), hole mobility in silicon ($1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), mechanical properties of Kevlar (Young's modulus = 130 GPa, tensile strength = 4 GPa), and actuation stress of skeletal muscle (*ca.* 0.35 MPa). Thus it is obvious that there is room for improvement in the properties of these polymers. This could be achieved by a combination of these polymers with materials whose properties exceed those of the polymers. An ideal candidate for such a material is carbon nanotubes (consisting of sp^2 hybridised carbon arranged into tubular structures) which have attracted enormous attention due to their phenomenal properties (see refs. 10, 33 and 63-66 for recent reviews). Thus combining polymers with carbon nanotubes in composites could offer the enticing prospect of materials with enhanced functionality compared to polymers. This paper reviews the main properties of electroactive polymers and carbon nanotubes, and explores the progress which has been made with enhancing the properties important for (intelligent) materials applications.

2. Carbon nanotubes

Carbon nanotubes (buckminsterfullerenes) are hollow cylinders with diameters ranging from *ca.* 0.4 (for single-walled carbon nanotubes, SWNTs) to *ca.* 100 nm (for multi-walled carbon nanotubes, MWNTs) with lengths on the micrometer scale. Let us briefly touch upon some of the main disadvantages of carbon nanotubes. (i) Standardisation: carbon nanotubes are not a standardised product (unlike most polymers), *i.e.* their properties and molecular structure depend on both the production method and manufacturer. (ii) Controlled synthesis: (to the best of my knowledge) it is not possible to completely control the chemical and electrical properties of carbon nanotubes at the point of assembly (synthesis). At best, the diameter range can be controlled during synthesis, yielding (during SWNT synthesis) a mixture of single-walled carbon nanotubes with semi-conducting and metallic properties. (iii) Processability: carbon nanotubes are mostly produced with defects, impurities, embedded catalyst and are bundled (or aggregated). They are not easily dispersed in most solvents due to their hydrophobic nature.

The main properties of carbon nanotubes are summarised in Table 1. In order to determine the properties of single carbon nanotubes, or for processed materials such as networks and fibres a certain degree of processing is necessary to overcome the processability issue. For example, individual carbon nanotubes can be fabricated through patterned (chemical vapour deposition) growth^{67,68} or selected using a manipulation tool.^{30,69-72} Two main methods are in use for the processing of carbon nanotubes: (i) a solution based approach (involving nanotube dispersions) for organising nanotubes into networks,⁷³⁻⁷⁷ or wet spinning of fibres;^{19,29,78,79} and (ii) patterned growth of nanotube networks⁸⁰⁻⁸² or forests of aligned nanotubes enabling dry spinning into fibres^{31,83,84}

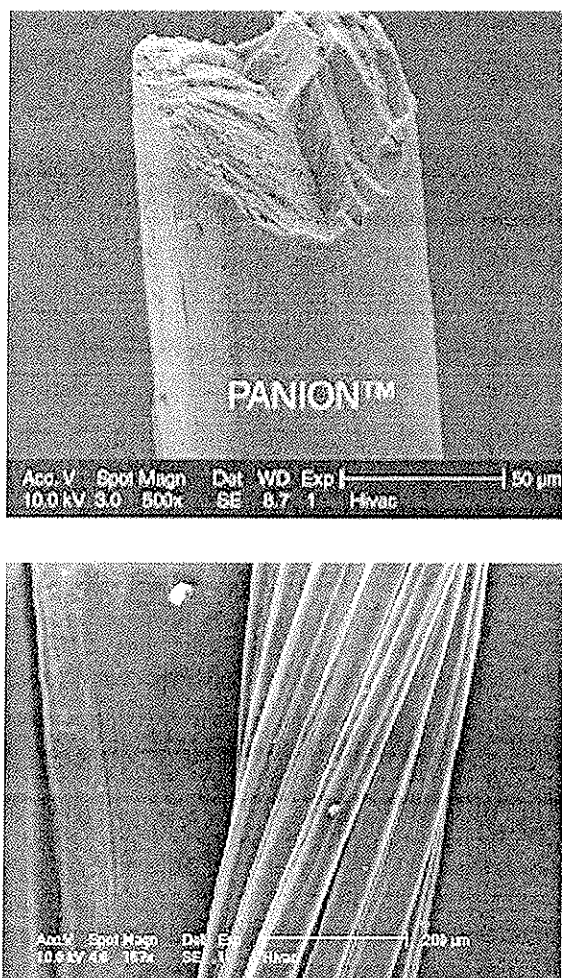


Fig. 1 Scanning electron microscopy images of PANION™ fibre (top) and yarn (bottom). (Reprinted with permission from W. Lu *et al.*, *Science*, 2002, 297, 383. © Copyright 2002 Santa Fe Science and Technology.)

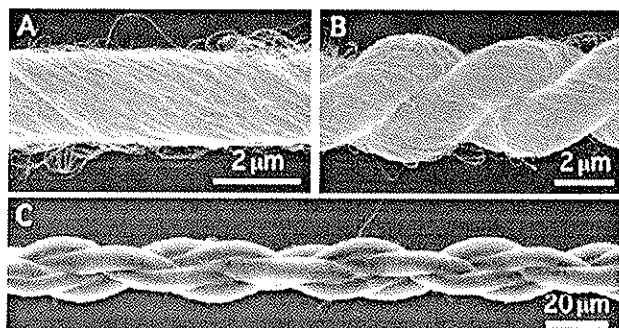


Fig. 2 Scanning electron microscopy images of (A) single, (B) two-ply, and (C) four-ply MWNT yarns. (Reprinted with permission from M. Zhang *et al.*, *Science*, 2004, 306, 1358. © Copyright 2004 American Association for the Advancement of Science.)

(see Fig. 2). The latter also allows the drawing of 5 cm-wide transparent and conductive nanotube sheets.⁸⁵

Metallic SWNTs with ideal contacts are ballistic conductors for which the conductance should approach the quantum limit $G = 4e^2/h$, corresponding to a resistance $R \approx 6.5 \text{ k}\Omega$.⁸⁶ Dai and co-workers¹⁷ obtained $R \approx 32 \text{ k}\Omega$ at 290 K for a metallic SWNT ($l = 4 \text{ }\mu\text{m}$, $d = 1.7 \text{ nm}$), yielding a conductivity of $0.9 \times 10^6 \text{ S cm}^{-1}$ (see Table 1). This should not be considered a limiting value, as significantly larger conductivities should be achievable for thinner and longer ideal metallic SWNTs. In addition it has been demonstrated that individual semi-conducting SWNTs exhibit excellent transistor characteristics ($I_{\text{ON}}/I_{\text{OFF}} \approx 10^6$).⁸⁷ However, these devices cannot be prepared through controlled (or selective) synthesis. Using carbon nanotubes organised into a network is a way around the synthesis problem as the properties then depend on all of the nanotubes (semi-conducting and metallic). However, this comes at a cost as the properties are reduced by several orders of magnitude (conductivity *ca.* 10^3 S cm^{-1} , transistor characteristic $I_{\text{ON}}/I_{\text{OFF}} \approx 10^4$).^{18,74,81} The conductivity of nanotube fibres is similar to that of the nanotube network, but is still several orders of magnitude below the possible maximum (ballistic transport). Other characteristics include current carrying capacity ($1 \times 10^9 \text{ A cm}^{-2}$),²³ carrier mobility ($10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)²¹ and room temperature thermal conductivity ($>10^3 \text{ W m}^{-1} \text{ K}^{-1}$).⁸⁸

The generally accepted values for the mechanical properties of individual SWNTs ($Y \approx 1 \text{ TPa}$, $T \approx 30 \text{ GPa}$)²⁶ and MWNTs ($Y \approx 0.61 \text{ GPa}$, $T \approx 37 \text{ GPa}$)³⁰ are impressive, while the accepted value for the Young's modulus of SWNT bundles is somewhat smaller (640 GPa).^{27,28} Processing nanotubes into fibres using various spinning approaches results in properties ($Y = 80 \text{ GPa}$, $T = 1.8 \text{ GPa}$)²⁹ which are an order of magnitude lower than those of single carbon nanotubes. Baughman *et al.* reported the first demonstration of nanotube actuation, based on SWNTs,⁸⁹ with the current maximum isometric stress being *ca.* 26 MPa .^{33,90} Recently, pneumatic actuation,⁹¹ MWNT based actuators,⁹² and fast actuation and charge responses⁹³ have also been demonstrated.

Optical activity should be inherent to most carbon nanotubes. This can be seen as follows: each individual carbon nanotube is uniquely specified by a chiral vector (defined in terms of graphene sheet unit vectors $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where

n and m are integers) and a chiral angle (defined as the angle between graphene sheet unit vector \vec{a}_1 and the chiral vector \vec{C}_h). See ref. 66 for complete details on the unique specifications of nanotubes. Taking symmetry aspects into consideration it can then be argued that carbon nanotubes for which $n \neq m$ and either $n \neq 0$ or $m \neq 0$ should exhibit optical activity. However, the optical activity is extremely difficult to investigate as the synthesis of nanotubes cannot be controlled. A theoretical treatment of chirality effects in carbon nanotubes was reported by Ivchenko and Spivak.⁹⁴

Thus it is clear that properties of carbon nanotubes surpass those of the electroactive polymers. The challenge is to incorporate carbon nanotubes into polymer composite materials and achieve enhanced properties.

3. Polymer-carbon nanotube composite

Considerable effort is being directed towards combining polymers and carbon nanotubes into composites with unprecedented mechanical and electrical properties. The following composite preparation methods are in use: functionalisation (non-covalent⁹⁵ and covalent⁹⁶), *in-situ* polymerisation,⁹⁷ electrochemical deposition,⁹⁸ direct mixing,⁹⁹ Latex technology¹⁰⁰ and intercalation.⁷⁵ See also the recent comprehensive overviews on mechanical reinforcement by Coleman *et al.*¹⁰¹ and on conductive composites by Koning and co-workers.¹⁰² Coleman noted that the best reinforcement was observed by Kumar *et al.*¹⁰³ using *in-situ* polymerisation of poly(*p*-phenylene benzobisoxazole) in the presence of SWNTs, while Koning concluded that direct mixing⁹⁹ is the easiest method for achieving conductivity in composites.

Let us now assess the progress which has been made with incorporating carbon nanotubes and electroactive polymers into composites. At present most research involves mainly polyanilines, with a smaller number of studies investigating polypyrroles and polythiophenes.

The essence of a good composite material lies in the interaction between the polymer and the carbon nanotubes. Maser and co-workers⁹⁷ and Smith's group¹⁰⁴ established that composites (in powder form) prepared by *in-situ* polymerisation of aniline in the presence of MWNTs enhanced the electronic properties, which were attributed to interactions between the PAN quinoid unit and the MWNT surface. During *in-situ* polymerisation the nanotubes are thought to guide the growth of the aniline, thereby acting as molecular templates. Maser and co-workers¹⁰⁵ proposed that this facilitates efficient π - π interactions between the PAN and the nanotubes, having a similar effect to that observed by in het Panhuis *et al.* in the absorption of a phenylenevinylene derivative,¹⁰⁶ and fully-sulfonated polyaniline (fully-PMAS),¹⁰⁷ onto nanotubes. Variations of this method include *in-situ* polymerisation of aniline in the presence of surfactant stabilised MWNTs,^{108,109} covalently-functionalised MWNTs,¹¹⁰⁻¹¹² a SWNT network,¹¹³ and an aligned MWNT forest.¹¹⁴ In a recent report, Cheng and co-workers sulfonated a PAN/MWNT composite (prepared by *in-situ* polymerisation) resulting in a water soluble material.¹¹⁵

Maser's group showed that composite powder in the non-conducting emeraldine base (EB) form could be easily

processed into supported¹⁰⁵ and free-standing films.¹¹⁶ In turn, these films could be easily converted into the (conducting) emeraldine salt (ES) form by exposure to HCl vapour,¹¹⁶ whereas composite films in the conducting ES form are also easily prepared by acid doping of the EB solution,¹¹⁷ or by facile preparation of an ES solution,¹¹⁸ prior to processing (see Fig. 3).

Alternative methods involve adding carbon nanotubes to a solution of EB, followed by processing into a film and doping with HCl^{104,119} or by adding EB solution onto a SWNT network followed by soaking in HCl,¹²⁰ while Li and co-workers reported the electrochemical polymerisation of aniline in the presence of a solution-stabilised SWNT.¹²¹

In an important recent development, Spinks *et al.* processed a solution of PAn and SWNTs into fibres using a wet spinning process.^{52,122} Other methods involve coating of hollow PPy

fibres with PAn/SWNTs¹²³ and dyeing textile yarns with fully-PMAS/SWNT using a conventional dye process.¹²⁴

The enhancements in properties achieved by combining carbon nanotubes (CNTs) with polyaniline are summarised in Table 2. Maser and co-workers¹⁰⁵ showed that the electrical conductivity of a composite consisting of non-conducting polyaniline (EB form) could be enhanced by nine orders of magnitude due to the presence of carbon nanotubes during *in-situ* polymerisation. In general an enhancement can be expected if the conductivity of carbon nanotubes is higher than that of the polymers, and, more importantly, if the loading of nanotubes is above the percolation threshold (the amount needed to form electrical pathways through the sample). For polymer blends the percolation threshold for nanotubes can be as low as 0.001% by volume.⁹⁹

Chen's group established that strong coupling between the carbon nanotubes and the polymer enhances the average localisation length and the electronic properties of the composites.¹²⁵ This is responsible for the carbon nanotube's gradual control of electronic transport with increasing carbon nanotube loading. The room temperature conductivities of pure carbon nanotubes and pure PAn were 1.1×10^{-2} and 2 S cm^{-1} , respectively. They established that the conductivity of conducting polyaniline could be enhanced by one order of magnitude with 10% MWNT loading and two orders of magnitude with 25% loading. Similar results were obtained by Zhang *et al.*¹⁰⁸ The observed enhancement is approaching the limit as determined by the individual conductivities of the constituents. These results are in excellent agreement with the expected enhancement based on the properties in Table 1 (although the absolute values are considerably smaller). Similar considerations apply for the enhancement in conductivity of fibres. For example, good electrical conductivity (716 S cm^{-1}) has been reported for PAn fibres containing 0.76% SWNTs.⁵²

Spinks and Wallace^{52,122} have investigated the mechanical and actuation properties of PAn/SWNT fibres. The Young's modulus of fibres consisting of a polyaniline leucoemeraldine base and SWNTs were enhanced from 2.6 to 6.1 GPa with 2% SWNT loading while the tensile strength increased from 116 to 229 MPa.¹²² The enhancement was attributed to reduced fibre porosity, and to interactions between the polymer and the nanotubes. The resultant Young's modulus (Y) of composites can be analysed by the rule of mixtures (see, for example,

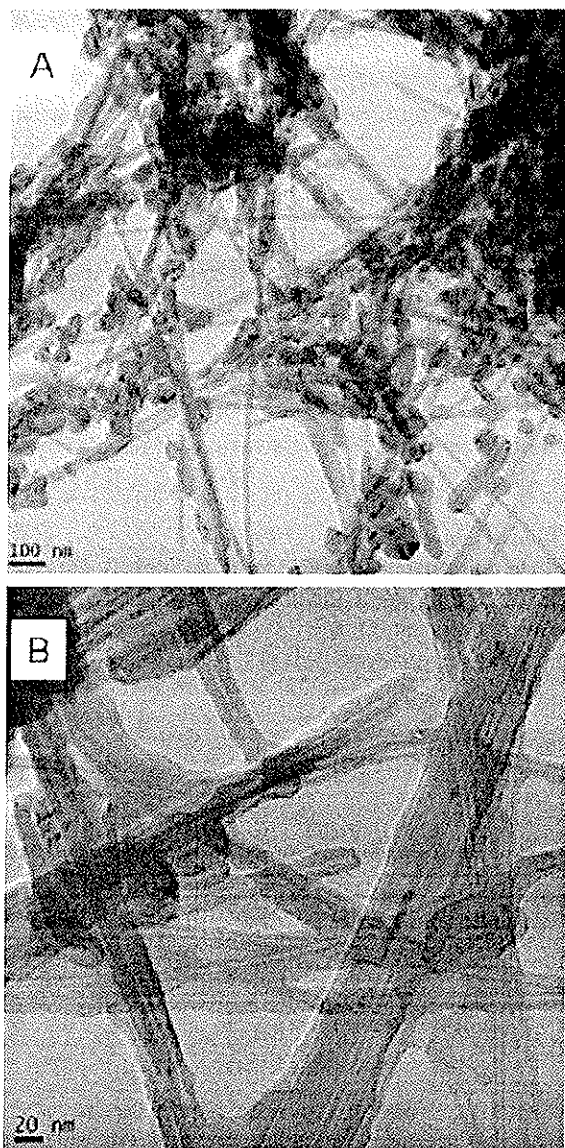


Fig. 3 Transmission electron microscopy images of polyaniline-MWNT composite in emeraldine salt form. (Reprinted with permission from M. in het Panhuis *et al.*, *J. Phys. Chem. B*, 2005, 109, 22 725. © Copyright 2005 American Chemical Society.)

Table 2 Summary of polyaniline/carbon nanotube composite properties displayed for processed materials (pressed pellets, films, fibres and textiles). EB, ES, LEB, PAn, PMAS, Y and T denote polyaniline emeraldine base, polyaniline emeraldine salt, polyaniline leucoemeraldine base, polyaniline, fully-sulfonated polyaniline, Young's modulus and tensile strength, respectively

Property	Material	Enhancement (compared to polymer)
Electrical conductivity	Pellet: EB/MWNT ¹⁰⁵	9 orders of magnitude
	Pellet: ES/MWNT ¹²⁵	2 orders of magnitude
	Fibre: LEB/SWNT ¹²²	>1 order of magnitude
	Textile: PMAS/SWNT ¹²⁴	4 orders of magnitude
Mechanical	Fibre: ES/SWNT ⁵²	T : 170 to 255 MPa
	0.76% CNT content	Y : 3.4 to 7.3 GPa
Actuation	Fibre: ES/SWNT ⁵²	90 to 120 MPa (isotonic stress)

ref. 75) defined as $Y = (Y_1 - Y_2)V_f + Y_2$, with Y_1 , Y_2 the moduli of components 1 and 2, respectively, and V_f the volume fraction of phase 1. Based on the information in ref. 122, a loading fraction of 2% SWNT corresponds to $V_f = 0.98\%$. Assuming the nanotube bundles to be phase 1, the rule of mixtures predicts that the modulus should be 8.8 GPa using the accepted value, $Y = 640$ GPa, for SWNT bundles (see Table 1).

In further work⁵² these results were significantly improved upon by using fibres consisting of polyaniline emeraldine salt and SWNTs (bundles). The Young's modulus was enhanced from 3.4 to 7.3 GPa for a loading fraction of 0.76%, while tensile strength improved from 170 to 255 MPa (see Fig. 4). The rule of mixtures approach would predict that the modulus should be 7.9 GPa, which is within 10% of the measured value. Spinks *et al.* suggested that this small difference indicates a high degree of separation, alignment and bonding of the carbon nanotubes (bundles) to the polymer.⁵²

The effect of carbon nanotubes on the actuation properties of PAN are as follows: strain decreases, while stress increases.^{52,123} Vice-versa, coating a carbon nanotube actuator with PAN improved the actuation strain.¹²⁰ This is what can be expected, based on the reported actuation strains for PAN actuators (<2%)³² compared to SWNT actuators (<0.7%).⁹¹ Addition of SWNTs to PAN fibres enabled stresses (under isotonic actuation conditions) of up to 120 MPa, an enhancement of 30 MPa compared to neat PAN fibres.⁵² As expected, the isotonic strain was reduced for the SWNT containing fibres (from 1.3%) to 0.85%. However, Spinks *et al.*⁵² noted that this is still considerably larger than the expected composite strain (0.57%) based on a rule of mixtures approach. They suggested that this was a result of improved charge transfer, thereby improving the efficiency of PAN actuation. These improvements are thought to be linked to the observed increased conductivity and electroactivity, which can be attributed to strong π - π interactions, which have been investigated by various groups.^{104,105,121,125}

Additional interesting developments for composites include retaining the polymer's optical activity in the presence of carbon nanotubes,^{117,118} a transparent and flexible PAN/CNT composite acting as a pH sensor,¹¹³ asymmetric capacitors using PPy/MWNTs and PAN/MWNTs allowing for

a capacitance of up to 320 F g⁻¹,¹²⁶ a glucose sensor based on PPy/MWNT,¹²⁷ and a single molecule device based on an individual SWNT coated with PPy.¹²⁸ Progress has been made for the charge mobility of composites, as demonstrated for a carbon nanotube network deposited on a polymer substrate.¹²⁹

4. Recommendations and conclusion

The rate of scientific publications in conductive polymers and carbon nanotubes has steadily increased since their discoveries in 1977¹³⁰ and 1991,¹³¹ respectively, to around 110 journal articles per week,¹³² indicating that the interest in polymers, nanotubes and their composites continues to grow.

The main areas of interest include electrical, mechanical, and actuation properties and are discussed below with particular focus on where carbon nanotubes can add value.

Electrical properties: it can be expected that composites based on 'metallic' polyaniline¹⁵ and individual carbon nanotubes should be able to push conductivity values towards (and possibly beyond) 1×10^4 S cm⁻¹, depending on the quality of the nanotubes, the state of nanotube debundling, and interactions between the polyaniline and the nanotubes. In addition, the phenomenal current carrying capacity of carbon nanotubes should have a significant impact on electronic textiles.

Mechanical properties: further enhancement of mechanical properties should be possible by accessing the superior mechanical properties of individual nanotubes over nanotube bundles (see Table 1). For example, the rule of mixtures approach predicts a Young's modulus of ca. 13 GPa for PAN fibres with a low volume fraction (1%) of individual carbon nanotubes, assuming $Y = 1000$ GPa for individual nanotubes and $Y = 3.4$ GPa for PAN fibres (see Table 1).

Actuation properties: it is clear that the addition of carbon nanotubes improves stress rates, although this comes at a cost for the strain rates. It is thought that improvement of composite conductivity and mechanical properties should have a significant impact on the actuation properties. Spinks *et al.*⁵² attributed their larger than expected actuation behaviour to a higher charge transfer efficiency, and suggested that this was linked to the higher composite conductivity. Thus the challenge is to combine 'metallic' polyaniline with individual single-walled carbon nanotubes.

In conclusion, this article has explored the possibilities for the use of carbon nanotubes in enhancing the polymer building blocks for intelligent materials applications. It is clear that carbon nanotubes have an important role to play in the improvement of properties. Significant progress has been made for mechanical and electrical properties for small carbon nanotube additions. However, improvement also comes at a cost as observed for the increase in actuation stress, coupled with a decrease in strain. The ultimate challenge is to produce composites which allow access to the properties of the individual carbon nanotubes.

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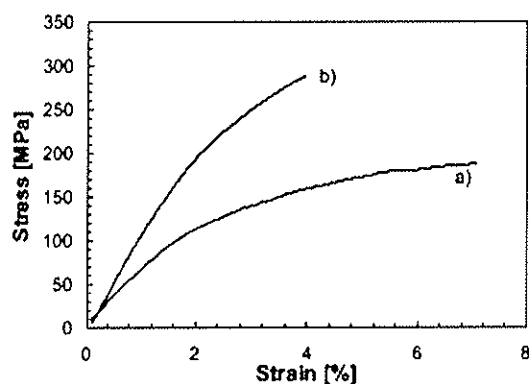


Fig. 4 Stress-strain curves (dry state) for (a) neat PAN and (b) SWNT-reinforced PAN fibres. (Reprinted with permission from G.M. Spinks *et al.*, *Adv. Mater.*, 2006, 18, 637. © Copyright 2006 Wiley-VCH, Germany.)

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